

Immobilization of TiO₂ nanoparticles on polymeric substrates by using electrostatic interaction in the aqueous phase

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Abstract

A new method for immobilization of TiO₂ nanoparticles on polymeric substrates was developed to facilitate photocatalytic purification of contaminated air and water. TiO₂ was immobilized by dipping a polymeric substrate, treated with polyvinyl chloride–polyvinyl acetate (PVC–PVA) copolymer and/or SiO₂, into a TiO₂/water suspension. The surface zeta potential measurement on TiO₂ and treated polymers implies that this method is based on an electrostatic interaction between positively charged TiO₂ and the negatively charged treated surface of the polymeric substrate. This method precludes the enwrapping of TiO₂ particles in binding components, which has been a drawback of conventional methods, and enables bonding of the TiO₂ nanoparticles on the substrate surface at high density. The TiO₂-immobilized nonwoven polyester (PES) prepared using this method exhibited high photocatalytic activity for decomposing the air contaminant toluene. Furthermore, this method was applicable to polypropylene (PP) nonwoven, polyethylene (PE) nets and PE and PP films. TiO₂ bonding was inhibited on PP by treatment with PVC–PVA copolymer and better TiO₂ immobilization was observed on SiO₂-treated PP.

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1. Introduction

Photocatalytic oxidation reactions on TiO₂ nanoparticles under UV-light irradiation have been used to decompose toxic substances in air [1–14] and water [15–20] since the beginning of 1990. For practical use of these reactions, TiO₂ nanoparticles must be immobilized on a suitable substrate, since the separation of nanoparticles from the reaction medium is difficult and costly. Hence, many techniques for immobilizing TiO₂ nanoparticles have been developed mainly for inorganic substrates such as glass [3,4,6,8,16,17], alumina [1,21], clay [3], and stainless steel [17]. These substrates are stable against active oxygen species (e.g. •OH and O₂•⁻), which appear on TiO₂ under UV-light irradiation. In contrast, much attention is required for immobilizing TiO₂ on polymer substrates, since most polymers are degraded by such active oxygen species.

TiO₂-bonded apatite and silica gel have been generally utilized to prevent degradation of textiles. Although detailed information is not available for these products, these materials have a role as both barrier layer and adsorbent. To immobilize on textiles, these products require a binder, but the latter frequently enwrap the TiO₂ particles when mixed with photocatalyst, and this reduces the activity of photocatalytic materials [22]. Aqueous silica sols are often used to produce a SiO₂ layer on inorganic substrates, but most of them are not applicable to polymers. Sol–gel reactions of alkoxysilane enable the formation of a layer of polysiloxane (SiO₂ network) on polymers. To date, only a few authors reported the use of this technique to make a barrier on a polymeric substrate [23–25].

In this paper, we report a new method for immobilization of TiO₂ nanoparticles on polymers. The sol–gel reaction of alkoxysilane was applied to produce a barrier layer of SiO₂ network, followed by coating with a thin layer of polyvinyl chloride–polyvinyl acetate (PVC–PVA) copolymer. TiO₂ was bonded in an aqueous phase using a physico-chemical interaction between TiO₂ particles and a dried surface coated

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with PVC–PVA copolymer. This interaction was found when commercially available polyester (PES) filter with special treatment was soaked in TiO_2 /water suspension. Analysis revealed that the surface substance is PVC–PVA copolymer and this finding was applied to immobilization of TiO_2 on polymers. Note that TiO_2 bonding does not occur with PVA. TiO_2 -immobilized PES nonwoven, prepared using the aforementioned method, exhibited high photocatalytic activity in decomposing the air contaminant toluene, and could be used as a filter for existing photocatalytic air purifiers. Furthermore, this method for TiO_2 immobilization could also be applicable to polypropylene (PP) nonwoven, polyethylene (PE) net, PE and PP films. TiO_2 bonding was inhibited by treatment with PVC–PVA copolymer and better TiO_2 immobilization was obtained on SiO_2 -treated PP.

2. Experimental

2.1. Photocatalysts

We mainly used the TiO_2 photocatalyst P25 (Japan Aerosil) with an average particle diameter of 21 nm and a specific surface area of $50 \text{ m}^2/\text{g}$. To confirm the applicability of the new immobilization method to another type of TiO_2 , we also used ST-01 (Ishihara Sangyo) with average particle diameter of 7 nm and specific surface area of $300 \text{ m}^2/\text{g}$. These photocatalysts were used as supplied without further treatments. An UV–vis photocatalyst BA-PW25 (Ecodevice) was used for elucidating the TiO_2 bonding mechanism.

2.2. Chemicals and polymeric substrates

We used a SiO_2 coating liquid SG COAT-EC-3570 (ECSEVEN, Tokyo), containing tetra-methoxysilane, tetra-ethoxysilane and catalysts, to form the SiO_2 barrier layer on the polymeric substrate. The coating liquid was used as purchased or after dilution with isopropyl alcohol (IPA). The formation of the SiO_2 network from alkoxysilanes is based on the sol–gel reaction.

The PVC–PVA copolymer was coated on the SiO_2 layer and then dried, to induce the bonding of TiO_2 in an aqueous suspension. We used Hishibond LR (Mitsubishi Resin) as a source of copolymer; this waterproofing substance for gutters is composed of PVC–PVA copolymer and organic solvents (70–80%). An aliquot of this mixture (gel) was dissolved in methylethylketone (MEK) and applied for the surface treatment. A solution of chitosan was used for elucidating the TiO_2 bonding mechanism.

We initially examined the immobilization of TiO_2 on Bonden 264 (Kurehatech), a nonwoven PES filter for air conditioners. The reinforcement material was removed before use. According to a data sheet for this filter, the butadiene-containing copolymer is mixed with PES. After we confirmed that our immobilization method is applicable, we tried to use it for other polymeric materials, such as PP nonwoven, which is used for cushion; PE net, which is used for building construction; and two kinds of polymeric thin films, namely

PE film, which is used as a transparent sack and oriented PP (OPP), which is used for packaging food products.

2.3. Procedure for immobilization of TiO_2 nanoparticles

The steps of the procedure for TiO_2 immobilization on the polymeric substrate described here are listed in Fig. 1. A $65 \text{ mm} \times 115 \text{ mm}$ sample of PES nonwoven was initially dipped in a SiO_2 coating liquid with or without dilution, after which the wet sample was centrifuged at 1500 rpm and then dried in a drying oven for 24 h at 80°C (dehydration of alkoxysilanes occurs during this period and a layer of SiO_2 network is formed on the fibers of the nonwoven PES). The dried sample was again dipped in a PVC–PVA copolymer solution in MEK. After a second centrifugation, the sample was left to dry in a draft chamber for more than 1 h and then put in a drying oven at 80°C for 1 h to accelerate drying and remove solvent. This dried sample was dipped in a TiO_2 aqueous suspension to enable TiO_2 nanoparticles to bond on fibers of PES nonwoven. The sample was dried by settling at room temperature over night. Heating at 80°C accelerated the drying. PE and PP samples were treated similarly.

2.4. Determination of photocatalytic activity

The photocatalytic activity of each TiO_2 -immobilized polymer sample was determined by a test method we established with a flow-type reactor (Fig. 2) to measure removal of toluene (1 ppm). This method is principally based on the Japanese standard JIS R 1701-1 [26] for measuring the performance of photocatalytic materials in NO_x removal. Gas chromatography with a flame ionization detector was used to analyze toluene content; the test gas initially contained 1 ppm toluene in purified air. A test piece of size $50 \text{ mm} \times 100 \text{ mm}$ was placed in the middle of the reactor. The gas to be analyzed flowed in a 5 mm layer between the quartz window and the top

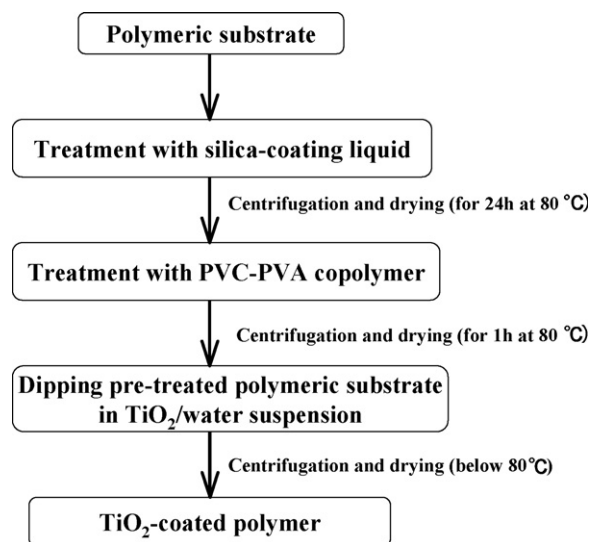


Fig. 1. Procedure for immobilization, of TiO_2 on a polymeric substrate using the electrostatic interaction in liquid phase.

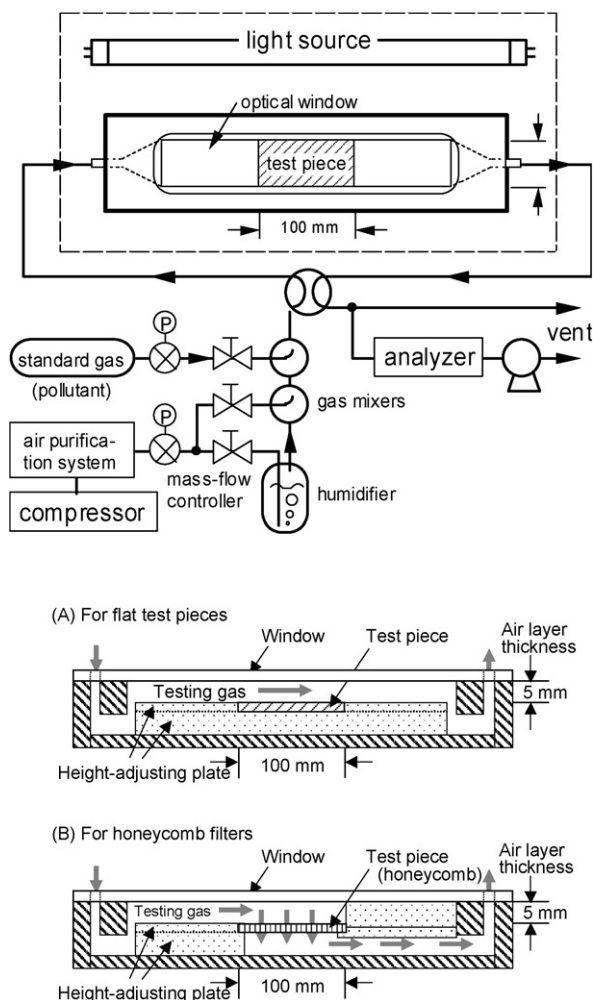


Fig. 2. The apparatus for determination of photocatalytic activity and two types of reactors for flat test pieces (A) and honeycomb filters (B). Standard gas: 1 ppm toluene in purified air. Analyzer: GC with FID.

of the test photocatalytic material. For the filter sample, the gas flowed from the top to the bottom (see the arrows in Fig. 2, reactor B). The photocatalytic reaction was carried out under a gas flow rate of 0.5 L/min at 25 °C; the relative humidity of the gas was 50%, and the light UV intensity was 1 mW/cm². The toluene concentration was determined and decreases were used as a measure of photocatalytic activity.

2.5. Characterization of immobilized TiO₂ on polymeric substrates

The immobilization of TiO₂ on polymeric substrates was characterized with field emission scanning electron microscopy (FE-SEM: TOPCON DS-720). Prior to measurement, each sample was coated with Pt/Pd by ion sputtering (HITACHI E-1030). To confirm that TiO₂ immobilization was based on electrostatic interaction, the surface zeta potential (mV) of particles for photocatalysts and polymeric substrates was measured, with and without surface treatment, with a PALS Zeta Potential Analyzer (Brookhaven Instruments Corp.). Polymers were crushed into fine particles using a cryogenic sample crusher (Yoshida Seisakusho JFC-300).

3. Results and discussion

3.1. Immobilized TiO₂ particles on PES nonwoven

The immobilized TiO₂ particles were uniformly distributed on the surface of the nonwoven PES fiber (Fig. 3A), and were densely packed (agglomerated) (Fig. 3B). Note that in conventional TiO₂ immobilization methods, other mixed substances added as a binder or a barrier component, often enwrap TiO₂ particles and this results in low photocatalytic activity [22]. In contrast, in the present method the TiO₂ particles are unwrapped; consequently, we expect higher photocatalytic activity. Moreover, the TiO₂ particles immobilized by the present method were strongly bonded and remained on the surface even after washing with water.

3.2. Effects of treatment conditions for PES nonwoven on photocatalytic activity

We measured the activity of the TiO₂-immobilized PES nonwoven sample in the dark and with UV-light irradiation (Fig. 4). In the dark ($t \leq 0$), the concentration of toluene varied within the fluctuation of analytical results, meaning that no strong adsorption by TiO₂ occurred. With UV-light irradiation, the concentration of toluene decreased very fast and then stabilized. We continued the measurement for TiO₂-immobilized PES nonwovens with UV-irradiation for 3 h (Table 1).

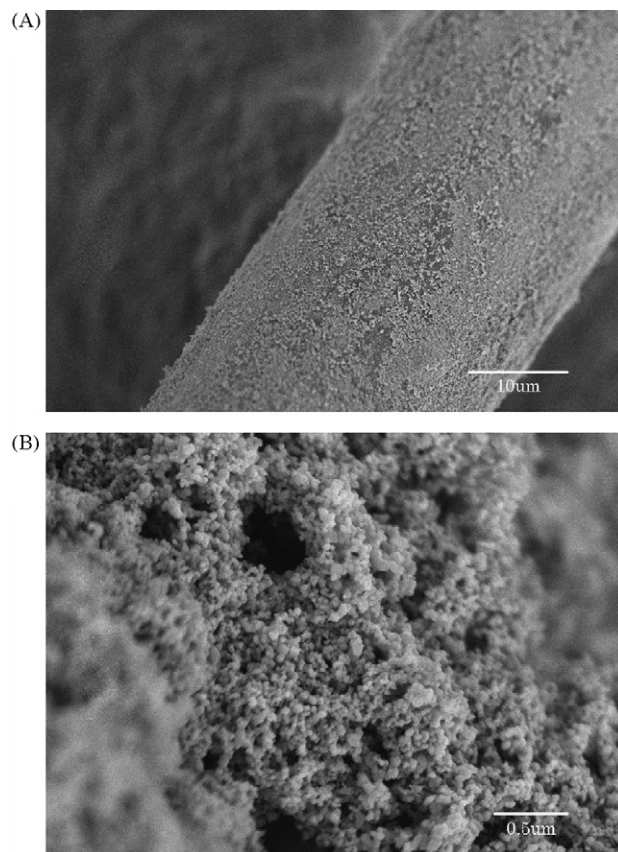


Fig. 3. SEM photographs of TiO₂ particles bonded on a fiber of PES nonwoven. (A) Magnification 2000 and (B) magnification 30,000.

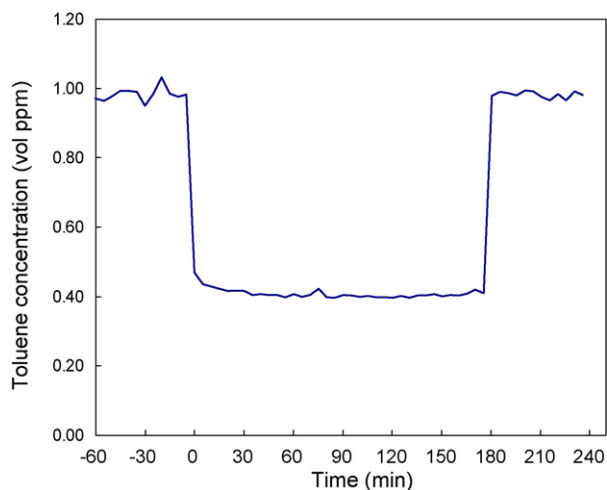


Fig. 4. Toluene concentration after passage of air over TiO_2 -coated PES nonwoven sample in a flow-type reactor. Air sampled before time 0 and after 180 min passed through the reactor without UV-light irradiation.

P25-immobilized PES nonwovens 1 and 2, respectively removed 58 and 53%, indicating good reproducibility of a method by treatment with SiO_2 and PVC–PVA copolymer. In addition, 49% toluene removal was obtained using a different photocatalyst, ST-01, deposited on the substrate by our new method. These results mean that the present method is applicable to various types of TiO_2 nanoparticles with different average particle diameter and different specific surface area. The method gives high photocatalytic activity that is sufficient for contaminant decomposition in air. Immobilized TiO_2 on PES was stable after 500 h irradiation with 4–5 mW/cm^2 UV lamp in the presence of VOCs in air. Moreover, we confirmed that TiO_2 -immobilized PES nonwoven is usable in water. Aqueous solutions of methylene blue and methyl orange (10 $\mu\text{mol}/\text{L}$) could be completely decomposed in the batch reactor under sunlight (average UV intensity: 2 mW/cm^2). In addition, about 60% bisphenol A in water (71.9 $\mu\text{mol}/\text{L}$) was decomposed in a circulating flow reactor under irradiation with two black lights (UV intensity: 5.5 mW/cm^2) for 5 h without TiO_2 particles peeling off from the substrate.

The effect of treatment conditions of PES nonwoven on the photocatalytic activity was further studied by changing the dilution (with IPA) ratio of the SiO_2 coating liquid used for

Table 1
Toluene removal by TiO_2 -immobilized PES nonwoven for the last hour of the 3 h measurements

Sample ^{a,b}	Removal (%)	Removal (supplied) ($\mu\text{mol}/\text{h}$)
PES nonwoven 1 (P25)	58.2	0.764 (1.312)
PES nonwoven 2 (P25) ^c	53.0	0.749 (1.414)
PES nonwoven (ST-01)	49.2	0.644 (1.308)

^a PES is the abbreviation of polyester.

^b TiO_2 immobilization was carried out with SiO_2 and PVC–PVA copolymer treatments.

^c This sample was prepared to confirm the reproducibility of present immobilizing method.

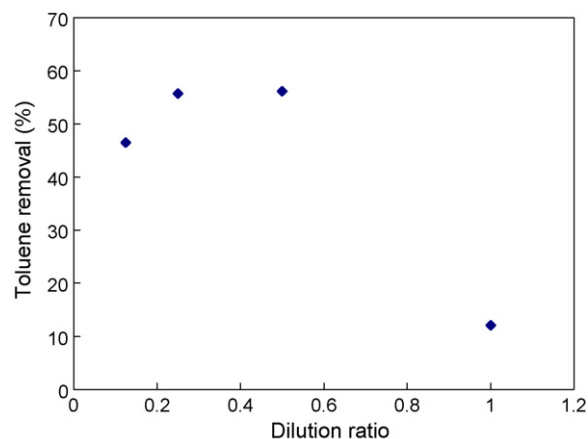


Fig. 5. Removal of toluene with various dilution ratios of silica coating liquid (a mixture of alkoxysilanes and IPA). Dilution ratio: volume of silica coating liquid/total volume of diluted solution.

making the barrier layer (Fig. 5). The activity was very low when we used pure SiO_2 coating liquid SG COAT-EC-3570 without dilution (ratio = 1). In this case, alkoxysilanes seem to be heterogeneously coated, since many lumps were observed on fibers of PES in SEM examination (not shown). The lumps may shield the UV light necessary for the excitation of TiO_2 and lower photocatalytic activity. Low dilution ratios, i.e., mixing with high amounts of IPA, also showed a tendency to decrease the activity (Fig. 5), and increased the softness of nonwoven, thus weakening the resulting photocatalytic material. Therefore, the silica coating liquid was used at a dilution ratio of 0.5. When the concentration of the PVC–PVA copolymer (including organic solvents) dissolved in MEK was increased, toluene removal slightly decreased (Fig. 6). Furthermore, lower concentrations of PVC–PVA copolymer resulted in increased softness of PES nonwoven. Hence, a solution of 25 g/L that gives high removal of toluene and moderate softness of the substrate was used for coating the copolymer layer on the SiO_2 -treated PES nonwoven. After investigating the effect of TiO_2 concentration in water suspension on the removal of toluene (Fig. 7), we used 5 g/L of TiO_2 /water suspension.

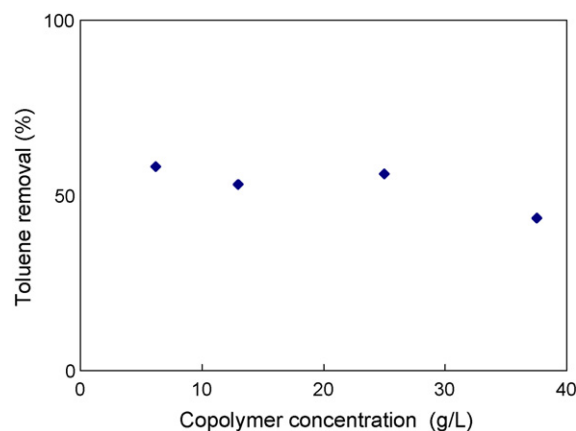


Fig. 6. Relationship between the removal of toluene and the concentration of PVC–PVA copolymer (including organic solvents) dissolved in MEK.

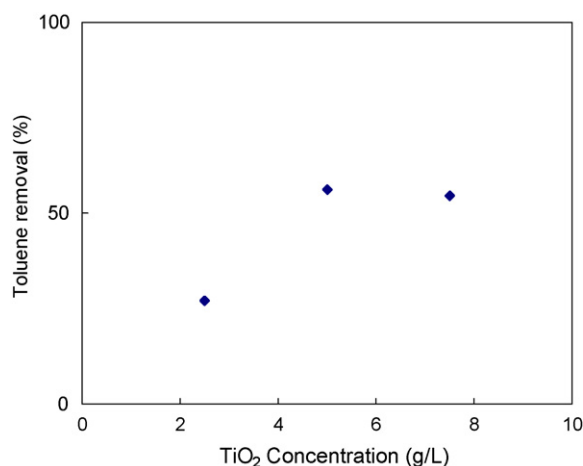


Fig. 7. The effect of TiO₂ concentration in the water suspension on toluene removal.

3.3. Applicability of the present TiO₂ immobilizing method to different polymers

Our TiO₂ immobilizing method fixes TiO₂ particles on the surface of polymeric substrates via physico-chemical interactions. We tested application of this method to immobilize TiO₂ on various polymers: PP nonwoven (used for cushion), PE net (used for building construction, for example in painting and keeping safety of workers and pedestrians), PE film (used for sacks), and OPP film (used for packaging food products).

The TiO₂ particles were homogeneously bonded on the surface of PE film treated with alkoxysilanes and PVC–PVA copolymer (Fig. 8), and the number of enwrapped particles, which in conventional immobilizing methods is high [22], was small here. The percentage of toluene removed by TiO₂-immobilized PE films was small (below 2%) compared with PES nonwoven (Table 2), but this is enough for use in such purpose as packaging. PE net exhibited better performance (13.3%) than the film. These results imply that the TiO₂ immobilizing method using PVC–PVA copolymer as a primer substance can apply to a variety of products made of PE.

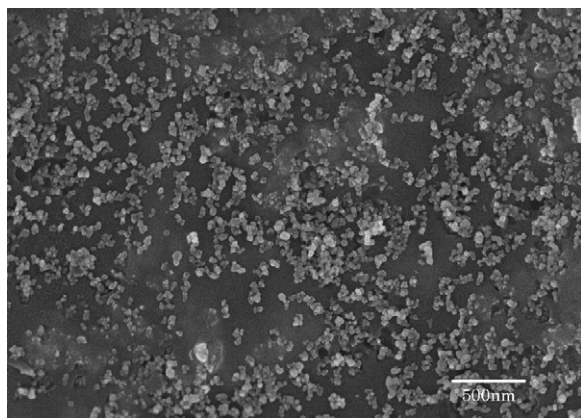


Fig. 8. SEM photograph of TiO₂ particles immobilized on PE film treated with PVC–PVA copolymer.

Table 2

Toluene removal by TiO₂-immobilized PP nonwovens, PE net and PE and PP films for the last hour of the 3 h measurements

Sample ^{a,b}	Removal (%)	Removal (supplied) (μmol/h)
PP nonwoven 1 (P25)	63.2	0.863 (1.365)
PE film	1.7	0.022 (1.276)
PE net	13.3	0.174 (1.303)
PP film	8.91	0.110 (1.216)

^a PP and PE are abbreviations of polypropylene and polyethylene, respectively.

^b TiO₂ immobilization on PP was carried out with SiO₂ treatment only and that for PE was carried out with PVC–PVA copolymer treatment.

On the other hand, PP nonwoven and OPP film treated with PVC–PVA copolymer, exhibited different results from PES and PE. TiO₂ particles were not bonded with the PVC–PVA copolymer coated on these PP-based samples. Instead, better TiO₂ immobilization was obtained when these samples were treated with SiO₂ only (Fig. 9). TiO₂ nanoparticles are uniformly distributed on SiO₂ network as well as coating on PVC–PVA copolymer. Table 2 presents the toluene removal performance for TiO₂-immobilized PP nonwoven and OPP film. The former photocatalytic materials are usable for air or water purification and the latter one for preserving the freshness of foods.

3.4. Bonding mechanism of TiO₂

We suppose that the bonding mechanism of TiO₂ for this method is similar to the first stages of TiO₂ thin film formation by the layer-by-layer self-assembling method based on ionic adsorption [27–34]. The surface of pre-treated polymers may work like a negatively charged polyelectrolyte and the TiO₂ particles would then be positively charged in the aqueous suspension [35] and would thus stick to the surface of the polymeric substrate. In order to confirm this mechanism, we measured the surface zeta potentials of polymers with and without pre-treatment as well as that of TiO₂ in NaOH/HCl solution containing 12.3% IPA. For measurement, solutions with pH ranging from 1.47 to 10.80 were prepared by changing NaOH/HCl molar ratio. IPA was added to prevent precipitation of particles and to form colloidal solutions. Although the value of

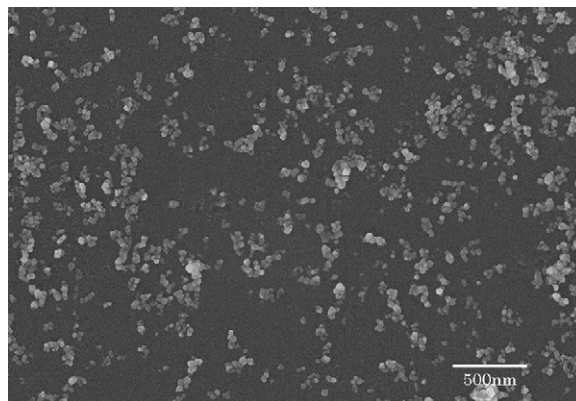


Fig. 9. SEM photograph of TiO₂ particles immobilized on OPP film treated with SiO₂ only.

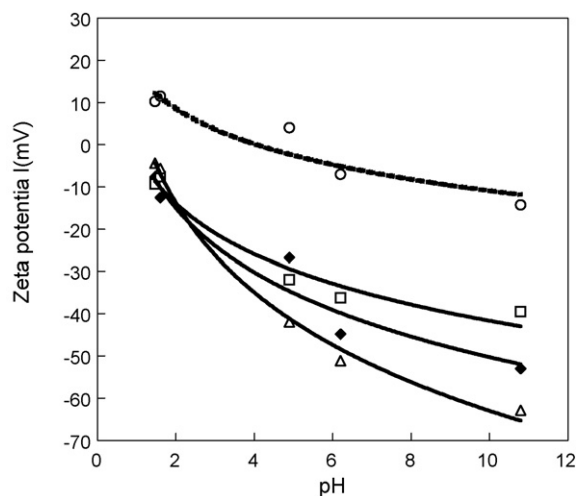


Fig. 10. Relationship between the pH of colloidal solutions and the surface zeta potential values for PES nonwoven samples with and without treatment and TiO_2 photocatalyst (P25). (\square) PES sample coated with PVC-PVA copolymer; (\blacklozenge) PES sample coated with SiO_2 ; (\triangle) PES sample without any treatment and (\diamond) TiO_2 (P25).

the surface zeta potential shifted to the positive side by adding IPA, the difference was smaller at lower pH range (15 mV at maximum under pH 6). All PES nonwoven samples exhibited negative zeta potential values and a sample coated with PVC-PVA copolymer exhibited the highest absolute potential from among the three PES samples (Fig. 10). The surface charge of P25 photocatalyst was positive at low pH and negative at higher pH (Fig. 10 dotted line); the isoelectric point was between pH 4 and 6. The measured pH of the colloidal suspension used for practical TiO_2 -immobilization was 4.1. Although the concentration of TiO_2 during practical immobilization was higher than that during zeta potential measurements (Fig. 7), we estimate from the data in Fig. 10 that the surface of P25 was positively charged. The positively charged TiO_2 electrostatically interacts with the negatively charged surface of pre-treated PES nonwoven and bonds there. The Cl substituent group in the structure of the PVC-PVA copolymer may be the cause of this bonding, since PVA does not bond with TiO_2 . We suppose that the PVC-PVA

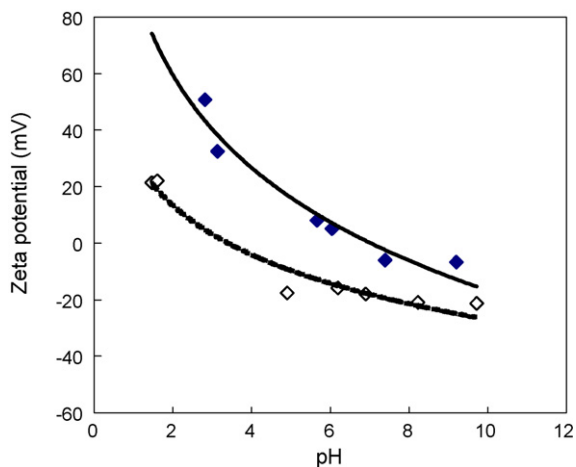


Fig. 11. Relationship between pH of the solution and the surface zeta potentials of BA-PW25 (\diamond) and chitosan (\blacklozenge).

copolymer provides adsorption sites on plain structural polymer chains such as PES and PE.

The importance of the electrostatic interaction was demonstrated using an UV-vis photocatalyst. The surface zeta potential values of BA-PW25 were all negative in the pH range above 4 (Fig. 11), and the pH of the colloidal suspension used for practical immobilization was 8.7. Under these conditions, BA-PW25 could not bond to negatively charged PES nonwoven treated with PVC-PVA copolymer, since both were negatively charged and had similar zeta potential values. We tried to use the polycation chitosan as an alternative primer, which may induce a positive charge on the substrate, and attempted to immobilize BA-PW25. BA-PW25 could bond on chitosan-coated PES, glass and paper at pH 8.7. Chitosan had higher surface zeta potential values than BA-PW25; its surface zeta potential at pH 8.7 was not higher than 0 mV, the isoelectric point, but it was higher than that of BA-PW25 (Fig. 11). The difference in zeta potential value between BA-PW25 and chitosan seems to have induced interaction and bonding. However, the bonding mechanism cannot be explained by the electrostatic interaction only, since BA-PW25 bonded on chitosan separated easily by touching with a finger on glass and paper substrates. Immobilization of BA-PW25 on chitosan-coated PES was good and the photocatalyst could remain on the surface even after washing with water.

Note that TiO_2 bonding on PP was prevented by the treatment with PVC-PVA copolymer and better TiO_2 immobilization was observed on SiO_2 -treated PP. The surface zeta potentials of PP samples with and without treatment were negatively charged, as were those of PES samples (Fig. 12). Difference between PES and PP was observable in the zeta potential value of the substrate without any treatment. Namely, the zeta potential of the PP samples without any treatment (Fig. 12) was positively shifted compared with that of PES without any treatment (Fig. 10). Fixation of SiO_2 on PES and PP may occur by “the anchoring” of negatively charged SiO_2 into small pores or ionic functional groups of the substrate. We

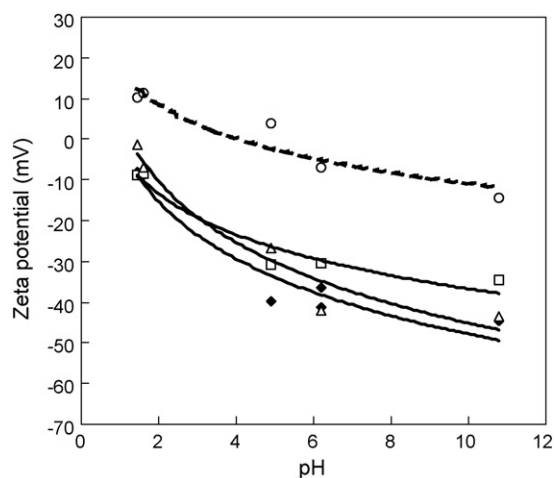


Fig. 12. Relationship between pH of the solution and the surface zeta potentials of PP samples with and without treatment and the TiO_2 photocatalyst. (\square) PP sample coated with PVC-PVA copolymer; (\blacklozenge) PP sample coated with SiO_2 ; (\triangle) PP sample without any treatment and (\diamond) TiO_2 (P25).

suppose the reason why TiO_2 bonding on SiO_2 -treated PP was prevented by the treatment with PVC–PVA copolymer as follows. The ionic adsorption strength of PVC–PVA copolymer against TiO_2 may be weakened by the presence of PP underneath or by smoothing a rough surface including small pores. A rough surface is generally thought to enable the bonding of particles on a substrate, and might be smoothed by the treatment with PVC–PVA copolymer in case of PP. The former may be connected with a molecular interaction between the polymer used as the substrate and the $\text{C}=\text{O}$ [36,37] or Cl ascribed to the copolymer through the porous SiO_2 layer. TiO_2 bonding to SiO_2 -treated PP may be explained by an ionic interaction between the negatively charged OH group of the SiO_2 -coated surface and the positively charged TiO_2 . In this case, the SiO_2 network with OH groups behaves like an ionomer [38]. The rough surface of SiO_2 -treated PP may also be linked with the bonding of TiO_2 .

4. Conclusions

A new method, which enables bonding TiO_2 nanoparticles on the surface of the polymeric substrate at high density and gives high photocatalytic activity, was developed. TiO_2 was immobilized on the substrate in aqueous phase by physico-chemical interaction between a primer substance coated on polymer (PVC–PVA copolymer and/or SiO_2) and TiO_2 . The surface zeta potential measurement on TiO_2 and treated polymers indicates that this method is principally based on an electrostatic interaction between positively charged TiO_2 and the negatively charged treated surface of the polymer substrate. This method precludes enwrapping of TiO_2 particles in binding components, which has been a drawback of conventional methods. TiO_2 -coated PES nonwoven prepared using this method exhibited high photocatalytic activity for decomposing the air contaminant toluene and was usable as a filter for existing photocatalytic air purifiers. Furthermore, this method was applied for coating TiO_2 particles on PP nonwoven, PE nets and PE and PP films. In the case of PP, treatment with PVC–PVA copolymer prevented TiO_2 bonding, and better bonding was observed for a SiO_2 -treated surface. Thus, the bonding mechanism of this method may be linked with the molecular interaction between a polymeric substrate and a coated substance or OH groups of a SiO_2 network.

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